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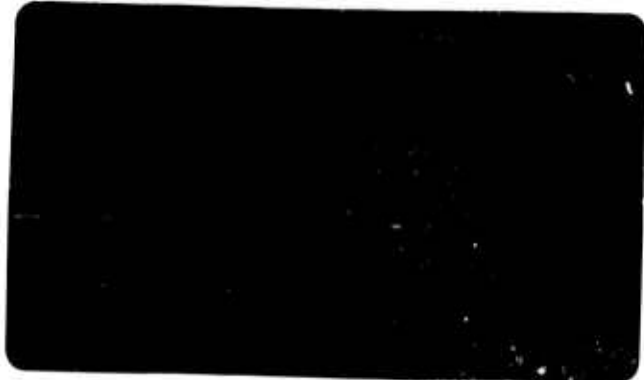


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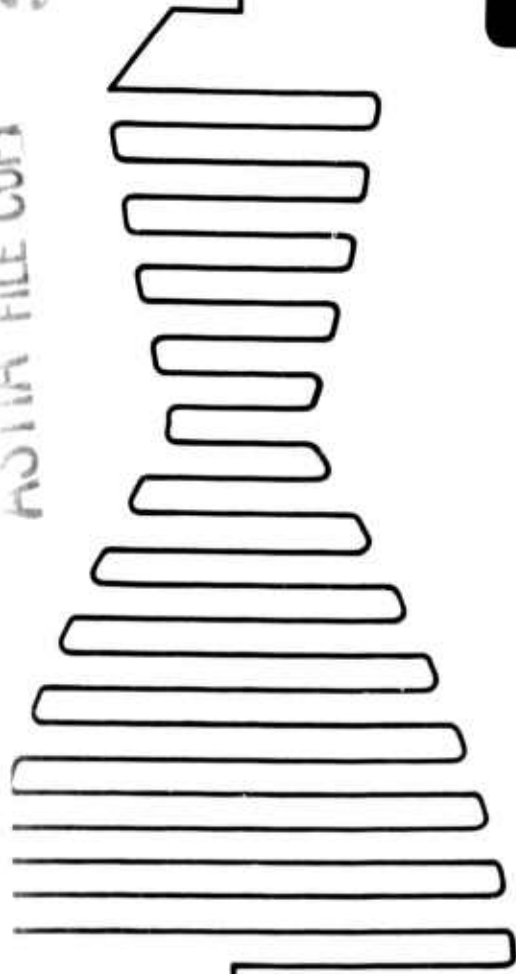
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R-3071-3

16

(Unclassified Title)

RESEARCH ON FLUORINE OXIDIZERS,  
QUARTERLY PROGRESS REPORT FOR  
PERIOD ENDING 15 DECEMBER 1961

Downgraded at 3 Year Intervals;  
Declassified After 12 Years.  
DOD Dir 5200.10

**ROCKETDYNE**

A DIVISION OF NORTH AMERICAN AVIATION, INC.

6633 CANOGA AVENUE  
CANOGA PARK, CALIFORNIA

Contract Nonr 3451 (00)  
ARPA Order No. 23-61  
Task 2, Item 1  
Project No. 9100  
G.O. 5983

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FOREWORD

This report was prepared by the Chemical Synthesis Group of the Research Department at Rocketdyne. This research effort is supported by the Advanced Research Projects Agency under Contract Nonr 3451 (00); ARPA Order No. 23-61, Task 2, Item 1, Project Code No. 9100.

The responsible scientist for this work is Dr. Emil A. Lawton. Dr. Walter Maya, Dr. H. Frederick Bauer, and Mr. David F. Sheehan are fulltime associates. Analytical support was furnished by Dr. B. L. Tuffly and Mr. I. Lysyj. We wish to thank Mr. D. W. Moore, NOTS, China Lake, California, for taking the NMR spectra in this work.

R-3071-3

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ii



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ABSTRACT

The solids obtained from the reactions of the  $\text{NF}_3\text{O}-\text{BF}_3$  complex with  $\text{Cl}_2\text{O}_7$  and  $\text{N}_2\text{O}_4$  were examined by NMR spectroscopy. No evidence was found for N-F compounds. Equally negative results were found for the reaction between  $\text{HClO}_4$  and  $\text{NF}_3\text{O}$ . The solid obtained from the interaction of antimony pentafluoride and  $\text{NF}_3\text{O}$  was shown to be largely  $\text{NOSbF}_6$ .

No reaction was obtained between  $\text{NF}_3\text{O}$  and aqueous <sup>KCN</sup>potassium cyanide. Although no reaction occurred between  $\text{NF}_3\text{O}$  and an aqueous solution of the sodium salt of nitromethane, when the reaction was run in the absence of water, all the  $\text{NF}_3\text{O}$  was consumed. The products of this latter reaction have not yet been determined.

The isolation of pure Compound A (a new interhalogen) by VPE is being attempted. A small peak has been obtained in the chromatogram that may be due to Compound A, but its size has precluded identification. Compound B has been obtained from the electric discharge of mixtures of <sup>Cl</sup>nitrogen trifluoride  $\text{NF}_3$  and chlorine. Compound B decomposes in glass to give  $\text{SiF}_4$  and  $\text{FCIO}_3$ , and is characterized by absorptions in the infrared at 719, 713 and 707  $\text{cm}^{-1}$ .

(Confidential Abstract)

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CONTENTS

|  |     |
|--|-----|
| Foreword . . . . .                         | ii  |
| Abstract . . . . .                         | iii |
| Discussion . . . . .                       | 1   |
| Chemistry of Trifluoramine Oxide . . . . . | 1   |
| New Interhalogens . . . . .                | 6   |
| Experimental Details . . . . .             | 10  |
| Chemistry of Trifluoramine Oxide . . . . . | 10  |
| New Interhalogens . . . . .                | 11  |
| Summary and Conclusions . . . . .          | 13  |
| References . . . . .                       | 15  |

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ILLUSTRATIONS

- |   |   |
|---|---|
| 1. Solid From $\text{NF}_3$ and $\text{SbF}_5$            | 2 |
| 2. $\text{NOSbF}_6$ From $\text{NOCl}$ and $\text{SbF}_5$ | 3 |
| 3. Infrared Spectrum of Compound B                        | 9 |

R-3071-3

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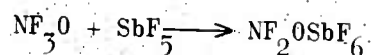
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DISCUSSION

CHEMISTRY OF TRIFLUORAMINE OXIDE

Reaction With Antimony Pentafluoride

The discovery that  $\text{NF}_3\text{O}$  forms a 1:2 complex with  $\text{BF}_3$  (Ref. 1), led to an investigation of the reaction of  $\text{NF}_3\text{O}$  with antimony pentafluoride (Ref. 2). The principal interest was to determine if the reaction took the following course:



If the stable white solid formed in this reaction were the salt  $\text{NF}_2\text{OSbF}_6$ , it would constitute the first example of a stable  $\text{NF}_2\text{O}^+$  ion. This ion has been postulated as the reactive intermediate in the additions of  $\text{NF}_3\text{O}$  to fluoro olefins (Ref. 3).

When antimony pentafluoride was allowed to react with an excess of  $\text{NF}_3\text{O}$  at room temperature, a vigorous reaction occurred and a white solid was formed. Its infrared spectrum (Fig. 1) showed no evidence for a compound such as  $\text{NF}_2\text{OSbF}_6$ , but indicated it to be mainly  $\text{NOSbF}_6$  with some possible nitrate impurity. Figure 2 shows the infrared spectrum of  $\text{NOSbF}_6$  obtained from the reaction between  $\text{NOCl}$  and  $\text{SbF}_5$  (Ref. 4), and comparison of the two spectra reveals them to be quite similar. Both spectra were taken in KCl pellets, prepared in a dry box.

R-3071-3

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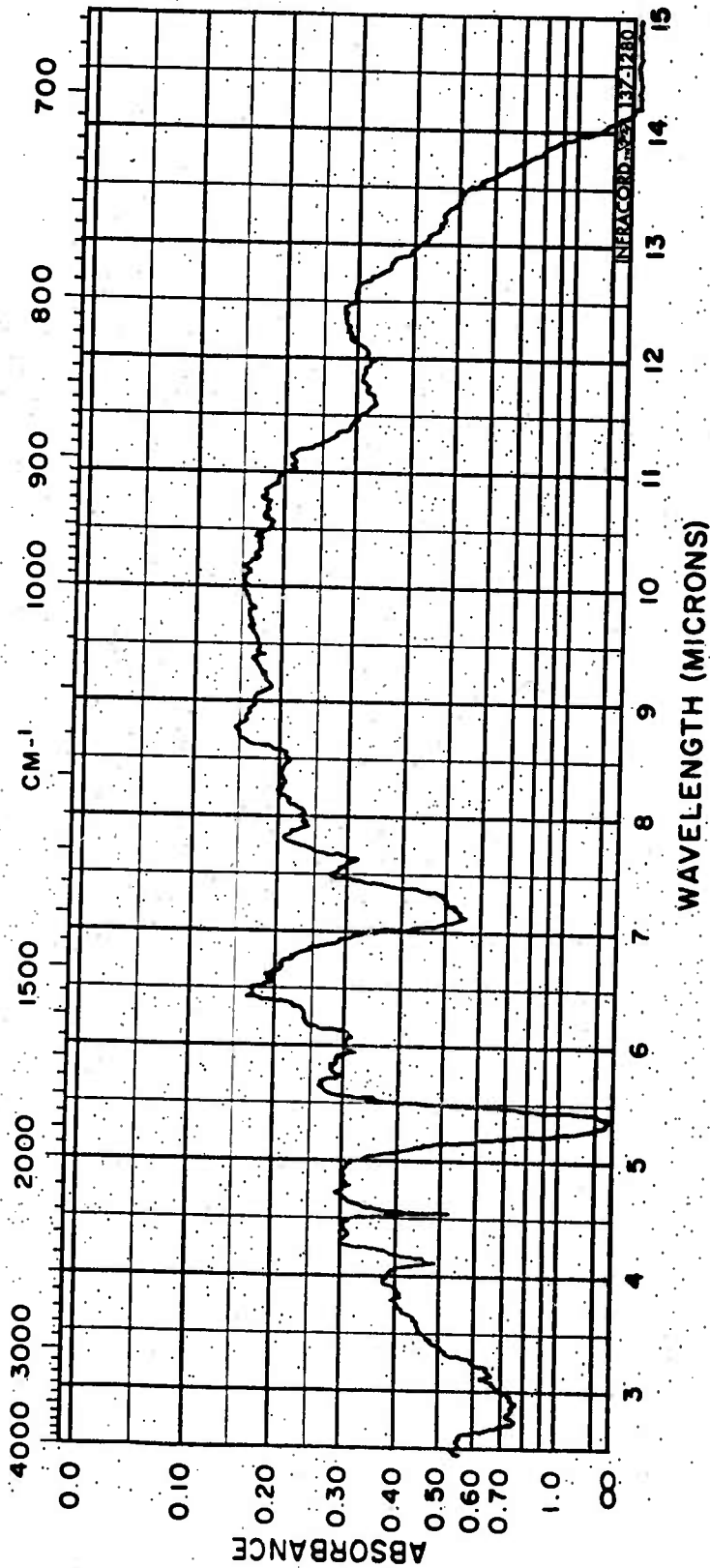


Figure 1. Solid From  $\text{NF}_3\text{O}$  and  $\text{SbF}_5$

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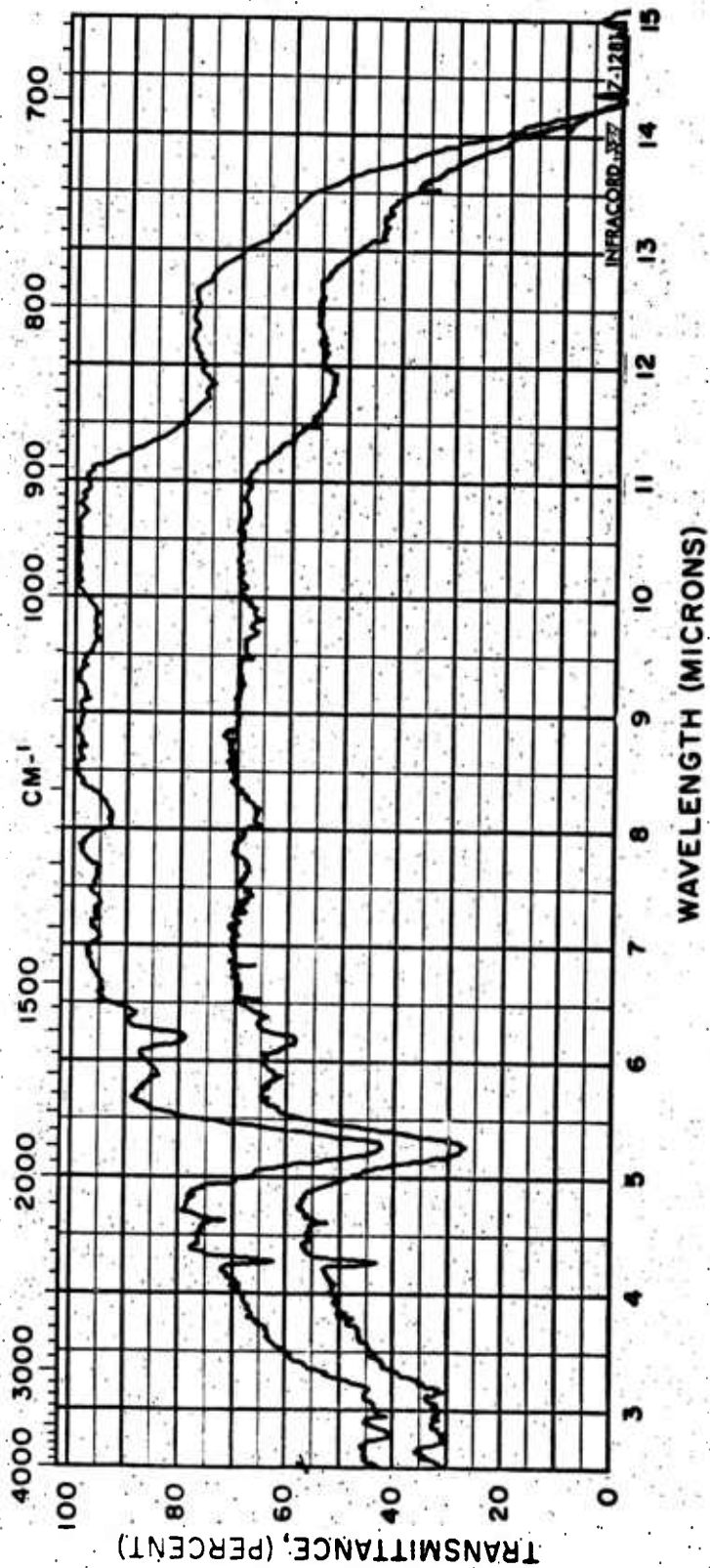


Figure 2. NOSC F<sub>6</sub> From NOSC and SbF<sub>5</sub>

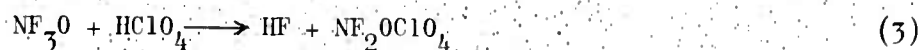
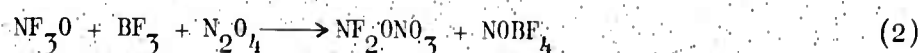
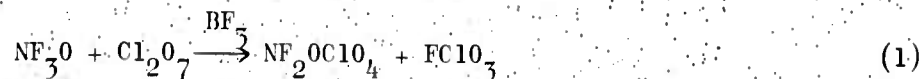
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It was not possible to obtain a vapor-pressure composition diagram of the  $\text{NF}_3\text{O}-\text{SbF}_5$  system because of the wide disparity of the physical properties of the two substances. Antimony pentafluoride melts at 7 C, while  $\text{NF}_3\text{O}$  has a boiling point of -89 C. Difficulty also was encountered in determining the stoichiometry of the reaction, both because the antimony pentafluoride tends to dissolve in the protective Fluorolube oil layer in the manometer; and because the white solids formed have about the same volatility as  $\text{SbF}_5$ . The amount of  $\text{NF}_3\text{O}$  consumed indicates reaction with two moles of  $\text{SbF}_5$ ; however, it is impossible to draw any conclusions in view of the experimental uncertainties.

Reaction with Chlorine (VII) Oxide,  
Nitrogen Dioxide and Perchloric  
Acid

In the previous report (Ref. 1), the following reactions were attempted:



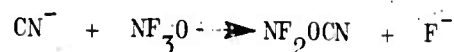
White solids obtained from reactions 1 and 2, and a nonvolatile liquid from reaction 3 were incompletely characterized; there was a possibility that they may have contained N-F substances.

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They have now been examined in the NMR, and no indications were found for the presence of N-F bonds. The only fluorine signal found was in the case of reactions 1 and 2, and were assignable to the  $\text{BF}_4^-$  ion.

Reaction With Potassium Cyanide

This reaction was attempted in an effort to extend the scope of the recently discovered addition of  $\text{NF}_3\text{O}$  to tetrafluoroethylene (Ref. 3). The following was the desired reaction, the formation of a C-O bond providing the driving force, as in the case of the addition to olefins:



When the reaction was attempted between  $\text{NF}_3\text{O}$  and aqueous KCN, all the  $\text{NF}_3\text{O}$  was recovered. This reaction will be repeated using nonaqueous solvents and employing the  $\text{NF}_3\text{O}-\text{BF}_3$  complex. The catalysis by  $\text{BF}_3$  may be a necessary element in all these reactions.

Reaction With Nitromethane

The reaction between the sodium salt of nitromethane and  $\text{NF}_3\text{O}$  is being studied for the same reasons as in the KCN case. The following is the desired reaction:

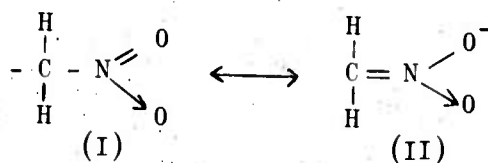


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The anion of nitromethane resonates between the two forms:



and several reactions are known in which the anion behaves as the carbanion (I), such as the formation of nitroalkanes from the reaction with alkyl halides, and the synthesis of trichloronitromethane by reaction with hypochlorous acid (Ref. 5).

When carried out in aqueous solution, no reaction occurred. However, when nitromethane was used as solvent, all the  $\text{NF}_3$  was consumed. This reaction is still under investigation to determine whether the desired addition took place.

#### NEW INTERHALOGENS

##### Compound A

During this quarter the main effort has been directed at obtaining pure Compound A. The synthetic procedure has been improved by employing conditions in the discharge that lead to increased gas ionization, thereby decreasing the amount of free chlorine obtained along with Compound A. Since  $\text{BF}_3$  does not form a complex with Compound A, it has been used in the purification procedures to complex undesirable side products such as  $\text{ClO}_2\text{F}$ . Despite these improvements, Compound A has not yet been obtained in the pure state.

R-3071-3

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Purification of Compound A by gas chromatography was attempted in a column packed with halocarbon oil on Kel-F powder (Ref. 6). Found were  $\text{SiF}_4$ ,  $\text{Cl}_2$ ,  $\text{ClO}_2$ ,  $\text{FCIO}_3$ , and an unidentified fraction too small to manipulate. Since the peak may be due to  $\text{ClO}_2\text{F}$  or Compound A, it is not yet clear whether Compound A is actually decomposing on the column or not.

The infrared spectrum of Compound A shows, in addition to the absorptions at  $732\text{ cm}^{-1}$  and  $787\text{ cm}^{-1}$ , another absorption at  $630\text{ cm}^{-1}$ . This latter absorption has p, q, and r branches which may be a result of an axial fluorine - chlorine stretching vibration  $A_1$ . While the parallel band for the axial fluorine - bromine stretch in  $\text{BrF}_5$  ( $A_1 = 690\text{ cm}^{-1}$ ) (Ref. 7) is at a higher frequency than the perpendicular band ( $E = 645\text{ cm}^{-1}$ ), in Compound A, these absorptions are reversed, with  $A_1 = 630\text{ cm}^{-1}$  and  $E = 732\text{ cm}^{-1}$ . This implies that if Compound A is  $\text{ClF}_5$ , the axial fluorine is further from the chlorine than are the other fluorines. The influence of the lone unshared electron pair in the proposed  $\text{ClF}_5$  molecule would have a greater tendency to crowd all five fluorines on one side of the central atom than in  $\text{BrF}_5$  because of increased steric crowding. The axial fluorine in  $\text{ClF}_5$  interacting more strongly with the other four fluorines, would then be forced further from the chlorine. The reversal in the order of the A and the E stretching frequencies in  $\text{BrF}_5$  and  $\text{ClF}_5$  would not be unreasonable.

Four preliminary experiments with radio-frequency electrodeless discharge of  $\text{NF}_3$  and  $\text{Cl}_2$  in a glass reactor resulted in the formation of reproducible, but small amounts, of Compound A and in one case  $\text{FNO}_3$ . The discharge could be maintained at pressures no greater than 5 mm and at relatively slow flowrates, ca 1 cc/min. A radio-frequency generator of greater power output will be necessary to increase the operating pressure of the system.

R-3071-3

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7

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Compound B

Compound B, previously considered as a possible binary N-F compound (Ref. 8), has been reproducibly made from  $\text{NF}_3$  and  $\text{Cl}_2$  along with Compound A. Compound B is the species previously referred to as the less stable of the two unknown compounds condensable at  $-142^\circ\text{C}$  and is characterized by absorption in the infrared at 719, 713, and  $707\text{ cm}^{-1}$  (Fig. 3). It reacts slowly with glass to give  $\text{SiF}_4$  and  $\text{ClO}_3\text{F}$ . Compound B formed a  $\text{BF}_3$  complex which could be easily separated from Compound A and other products. Thus, Compound B may be a new species containing chlorine and fluorine. The further investigation of Compound B has been temporarily set aside in favor of Compound A.

Because of the reactivity of Compounds A and B with glass, future work is planned in nonglass systems. To this end, an alumina and stainless-steel discharge cell is in fabrication and will be used in conjunction with a metal vacuum system. The use of high-purity alumina (99 percent  $\text{Al}_2\text{O}_3$ ) is indicated by the need for a nonconducting cell material resistant to attack by fluorine.

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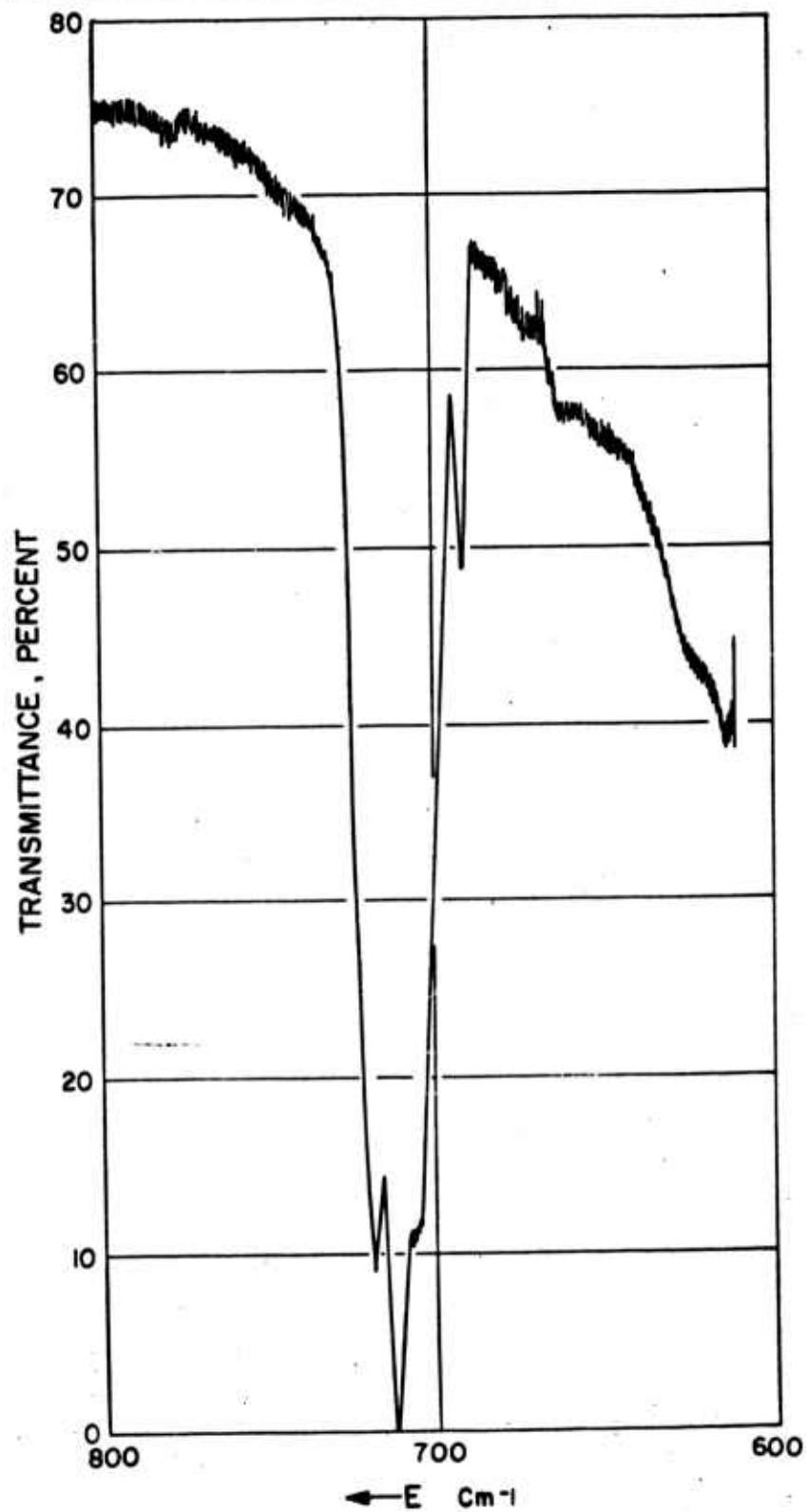


Figure 3. Infrared Spectrum of Compound 2

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EXPERIMENTAL DETAILS

CHEMISTRY OF TRIFLUORAMINE OXIDE

Reaction With Antimony Pentafluoride

Antimony pentafluoride (1.7 mmols) was allowed to come into contact with an excess of  $\text{NF}_3\text{O}$  (373 cc) at room temperature. A vigorous reaction occurred, and a white solid was formed. The solid weighed less than the starting  $\text{SbF}_5$  because of the absorption of the  $\text{SbF}_5$  in the Fluorolube layer in the manometer and to the volatility of the solid. The  $\text{NF}_3\text{O}$  consumed in the reaction (0.8 mmols) corresponded to a 1:2 reaction with  $\text{SbF}_5$ . The infrared spectra of the solid is shown in Fig. 1, taken in a KCl pellet. The solid was found to react with Nujol when ground in a dry box.

Reaction With Chlorine (VII) Oxide,  
Nitrogen Dioxide and  
Perchloric Acid

The experimental procedures were the same as described in the previous report (Ref. 1). The white solids were found to be somewhat soluble in nitromethane. Sulfur dioxide, carbon tetrachloride, and  $\text{Cl}_2\text{O}_7$  did not dissolve the solids, while diethylether reacted with them.

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Reaction With Potassium Cyanide

A solution containing 6.2 mmoles of KCN was allowed to stand overnight in contact with 1.8 mmoles of  $\text{NF}_3\text{O}$ . No reaction occurred, and all the  $\text{NF}_3\text{O}$  was recovered.

Reaction With Nitromethane

Trifluoramine oxide (29 cc) was left in contact with a solution containing an excess of nitromethane, made basic with NaOH, for two hours. Essentially all the  $\text{NF}_3\text{O}$  was recovered.

Nitromethane was left to stand for 24 hours in contact with NaOH. The clear yellow supernatant solution was then pipetted into an ampoule (2 ml), and exposed to 28 cc of  $\text{NF}_3\text{O}$ . After two hours, all the  $\text{NF}_3\text{O}$  had been consumed. The liquid is currently under investigation to determine if the desired reaction occurred.

NEW INTERHALOGENS

Compound A

A total of seven glow-discharge reactions employing  $\text{NF}_3$  and  $\text{Cl}_2$  were carried out. The samples submitted for gas chromatography were fractionated through a -112 C trap and condensed at -126 C. Only a single fractionation was carried out to minimize the reaction of Compound A with glass. Fractions recovered from the chromatographic column and identified were  $\text{SiF}_4$ ,  $\text{ClO}_2$ ,  $\text{Cl}_2$ , and  $\text{FClO}_3$ .

R-3071-3

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11

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The preparation of Compound A by radio-frequency electrodeless discharge was carried out in a glass reactor at 800 volts and 90 ma. Both straight-tube and concentric-tube arrangements of the discharge cell were tested with no observable difference.

Compound B

Compound B was synthesized along with Compound A and separated from  $\text{ClF}$ ,  $\text{ClF}_3$ , Compound A,  $\text{ClO}_2\text{F}$ ,  $\text{ClO}_2$ ,  $\text{NF}_3$ ,  $\text{Cl}_2$ , and  $\text{SiF}_4$  by the addition of excess  $\text{BF}_3$  and fractionation through  $-80^\circ\text{C}$ ,  $-112^\circ\text{C}$ , and  $-126^\circ\text{C}$  traps. The  $-112^\circ\text{C}$  trap contained some  $\text{SiF}_4$ ,  $\text{BF}_3$ , and Compound B. However, neither  $\text{BF}_3$  nor Compound B was observed in the  $-126^\circ\text{C}$  trap.

About 5 cc of Compound B exploded while at  $-196^\circ\text{C}$  in a U trap. The explosion was of sufficient force to destroy the U trap and the adjoining glass connections. The cause of the explosion is unknown.

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SUMMARY AND CONCLUSIONS

The reaction of  $\text{NF}_3\text{O}$  with antimony pentafluoride yields a white solid, shown to be largely  $\text{NOSbF}_6$ , rather than  $\text{NF}_2\text{OSbF}_6$ .

The solids obtained from the reactions of the  $\text{NF}_3\text{O}-\text{BF}_3$  complex with  $\text{Cl}_2\text{O}_7$  and  $\text{N}_2\text{O}_4$  have been shown by NMR and IR not to contain N-F compounds. Equally negative results were obtained for the reaction of  $\text{NF}_3\text{O}$  with  $\text{HClO}_4$ .

Trifluoramine oxide has been shown not to react with aqueous potassium cyanide. The reaction will be tried employing the  $\text{NF}_3\text{O}-\text{BF}_3$  complex in a nonaqueous medium.

Trifluoramine oxide did not react with an aqueous solution of the sodium salt of nitromethane; however, a reaction did occur when nitromethane itself was used as a solvent. This reaction is being investigated to determine whether new  $\text{NF}_2\text{O}$ -type compounds have been synthesized.

Compound A has thus far eluded efforts to prepare it in the pure state. Compound A does not form a  $\text{BF}_3$  complex, and  $\text{BF}_3$  has been used to complex unwanted side products in the synthesis, such as  $\text{ClO}_2\text{F}$ . Purification by gas chromatography is under study. A small unknown fraction has been obtained in the VPC column that may be caused by Compound A, but the fraction has been too small to identify.

R-3071-3

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Compound B has been obtained by subjecting mixtures of  $\text{NF}_3$  and  $\text{Cl}_2$  to the glow discharge at  $-78^\circ\text{C}$ . Compound B decomposes in glass to give  $\text{FClO}_3$  and  $\text{SiF}_4$ . It absorbs in the IR at 719, 713, and  $707\text{ cm}^{-1}$ . On one occasion, Compound B exploded with considerable force while in a U trap at  $-196^\circ\text{C}$ . The cause for the explosion is not known.

R-3071-3

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14

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